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NEW TECHNOLOGY FOR CONTROLLING NO_x FROM JET ENGINE TEST CELLS

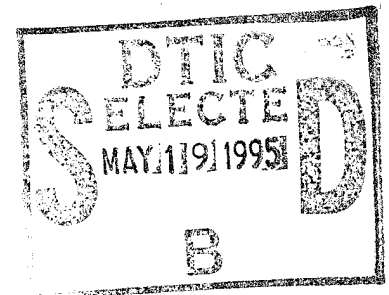
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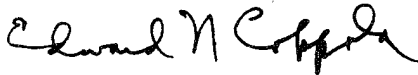
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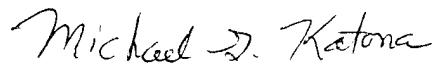


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13. ABSTRACT (Maximum 200 words) For some time the U.S. Air Force has been concerned with NOx emissions from jet engine test cells operated by the Air Force. While there are no regulations limiting the NOx emissions of these facilities, such regulations could develop in the near future and would pose significant problems for the Air Force because no available technology is suited for application to jet engine test cells. This report describes laboratory studies of a new NOx control process based on the surprising ability of barium oxide to rapidly capture NO, a process that could be ideally suited to controlling NOx emission from jet engine test cells. Thus, experiments were done in which a simulated exhaust gas containing NO was passed through a bed of either granular barium oxide or				
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barium oxide supported on high-strength alumina. Quantitative NO removals were achieved at space velocities ranging from 2010 to 28,000 v/v/hr, temperatures from 21°C to 610°C, oxygen concentrations of 1.1 to 15.3 percent, and initial NO concentrations from 94 to 1700 ppm. When NO₂ was present in the simulated exhaust, it was also removed. The barium oxide was able to capture NO and NO₂ in amounts up to at least 23.5 percent of its initial weight.

The practical implication is that NO_x emissions of a jet engine test cell could be controlled by replacing the acoustic panels now used to decrease the cell's emission of sound with a set of panel bed filters filled with barium oxide. These panel bed filters would also absorb sound, could fit in the space in the test cell now occupied by the acoustic panels, and would remove NO and NO₂ from the exhaust before it is discharged to the environment. This NO_x removal would occur spontaneously, without any actions by the personnel operating the test cell and without distracting them in any way from their normal tasks.

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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of this research project was to perform a laboratory-scale proof of concept evaluation of a new technology--sorption of NO_x during passage of exhaust gases through a bed containing barium oxide (BaO)--that was proposed to be applicable to the task of controlling NO_x emissions from jet engine test cells.

B. BACKGROUND

For some time the U.S. Air Force has recognized that NO_x emissions from jet engine test cells (JETCs) operated by the Air Force are, although a relatively minor fraction of the total NO_x emissions released during jet aircraft operations, a significant contribution (typically 10-20 tpy) to total NO_x released by facility stationary sources. Whereas no current regulations limit the NO_x emissions from these facilities, such regulations could develop and would pose a significant problem for the Air Force because no available technology is suited for application to jet engine test cells.

C. SCOPE

This report describes research done under DoD's Small Business Innovation Research (SBIR) program, Contract No. F08635-88-C-O263, "New Technology for Controlling NO_x." The Introduction of this report discusses the nature of the problem of NO_x emissions from jet engine test cells and explains why presently available or proposed NO_x control technologies are poorly suited for use on jet engine test cells. The experimental methods used in this research are summarized in Section III. Section IV describes bench-scale results arguing for the economic and technical feasibility of a new process for controlling NO_x emissions, the BaNO_x process.

D. METHODOLOGY

The experimental apparatus used was EER's Precision Gas Kinetics Flow System, which consists of three subsystems: gas blending, reactor, and analytical instrument train. Fischer Porter rotameters, calibrated by a wet test meter with nitrogen, were used to monitor the flow of gases for accurate mixing. A Matheson Mass Flowmeter was also used to verify flowrates. The reactor was a 0.75-inch OD x 0.68-inch ID stainless steel tube with inlet and outlet reducers of 0.25-inch OD x 0.18-inch ID tubing placed within the uniform-temperature-distribution area of a three-zone Thermcraft tube furnace. The BaO sorbent was configured inside the reactor to simulate a jet engine test cell configuration. Furnace temperatures were controlled with three CA

thermocouples (placed in the center of each zone) in a feedback system with three Lindbergh digital proportional

temperature controllers. Furnace temperatures were monitored with five CA thermocouples read by a Doric Digital Thermocouple reader at a resolution of 1°C. NO levels were measured with a Thermoelectron Chemiluminescent NO_x analyzer. A Teledyne O₂ analyzer was used to measure O₂ levels. Both analyzers had a precision better than 2 percent and were calibrated daily. The weight gain of the BaO sorbent was measured with a Mettler H54 balance.

E. TEST DESCRIPTION

Experiments were done in which a simulated exhaust gas containing NO was passed through a bed of either granular barium oxide or barium oxide supported on high-strength alumina. After calibration of NO and O₂ meters, the furnace was turned on and heated to a constant temperature. Gas flow was initiated and adjusted to desired values. A sample of the gas mixture was analyzed for initial NO and NO₂ concentrations. The gas mixture was then passed through the reactor and BaO bed, and the changes in NO and NO₂ concentrations were determined.

F. RESULTS

Quantitative NO removals were achieved at space velocities ranging from 2010 to 28,000 v/v/hr, temperatures from 21°C to 610°C, oxygen concentrations of 1.1 to 15.3 percent, and initial NO concentrations from 94 to 1700 ppm. When NO₂ was present in the simulated exhaust, it was also removed. Barium oxide was demonstrated to capture NO and NO₂ in amounts up to at least 23.5 percent of its initial weight, approximately 33 percent of the theoretical limit.

G. CONCLUSIONS

The capture of NO by BaO (apparently by initial formation of BaO₂) to form the nitrate appears to satisfy nearly all the requirements for a practical process to control NO_x emissions from JETCs. A NO_x control process based on this reaction could be retrofitted into an existing jet engine test cell without requiring any change in normal cell operation. Further, using this new NO_x control process would require little or no attention from the personnel operating the jet engine test cell. The single issue from an engineering perspective is that the pressure drop across the bed is about 4 inches of water, which may be excessive for the JETC. A major environmental concern in the use of barium compounds is the requirement that spent sorbent must be treated as a toxic material upon disposal, although regeneration of the sorbent in service would attenuate this liability.

H. RECOMMENDATIONS

As large-scale testing is necessary to determine the applicability of a control technology for reduction of NO_x emissions from jet engine test cells based upon the reaction of BaO with NO, we recommend implementation of a BaO filter as a field test for NO_x removal from a jet engine test cell. Apparatus could be set up similar to laboratory-scale experiment, using a slip-stream of gas from the test cell. Alternatively, acoustic panels (used to decrease the sound level emitted from the test cell) inside the test cell might be replaced with a set of panel bed filters filled with barium oxide granules.

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SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this research project was to conduct a laboratory-scale proof-of-concept evaluation of a new NO_x control technology applicable to controlling combustion-derived NO_x emissions from jet engine test cells (JETCs).

B. BACKGROUND

The exploration of new candidate technologies for NO_x control is important because the United States Air Force operates a number of JETCs, any or all of which are potentially subject to future regulation of the amount of NO_x they can emit.

Figures 1 and 2, quoted from Reference 1, show a typical jet engine test cell. Table 1 shows typical data from Reference 1 describing the NO_x content and other properties of the exhaust produced by typical engines in a test cell. (Some of the numbers in Table 1 are quoted directly from Reference 1, whereas others are calculated from data tabulated therein.)

The typical operation of a JETC is atypical. The cell sits idle much of the time, and during operation more time is spent in setup and disconnection than in engine operation. Time at any power setting is normally a few minutes--about the time it takes for the JETC to adjust to the exhaust temperature--so start-up artifacts of any control device used will dominate its net performance. An engine test is commonly conducted by operating the engine for several minutes at idle, at one or more fractional power stages, and at full power. Nearly all of the NO_x emissions result during the latter portion of the operation. Based on fuel consumption data for representative JETCs, a typical test cell will emit from 10 to 30 tons of NO_x per year.

The jet engine being tested in a test cell acts as a pump. The engine develops thrust and this force is directed down a long tube called the augmentor tube. This pumping action pulls in several volumes of ambient air, generally diluting the exhaust gas by a factor of three. As shown in Figure 2, the far end of the augmentor deflects the gas flow, and the path of the airflow may also include a perforated distribution plate or baffles, which serve as flow restrictions, regulating the amount of ambient air pumped through the system.

In older-style (water-augmented) cells, this has two important implications for NO_x control, one favorable, one unfavorable. The favorable implication relates to the fact that the many NO_x control technologies that treat the exhaust gas by putting it through a catalyst bed,

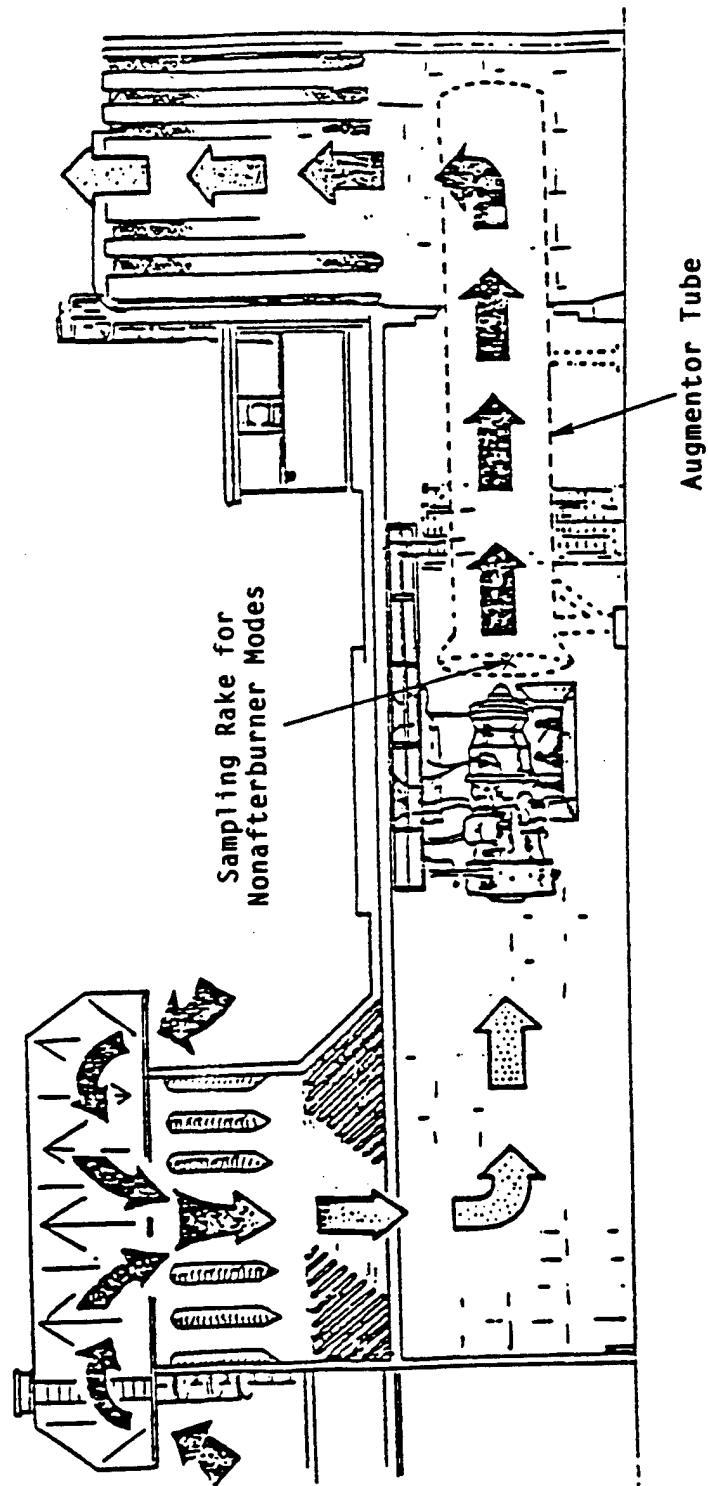


Figure 1. Test Cell Cross Section (quoted from Reference 1).

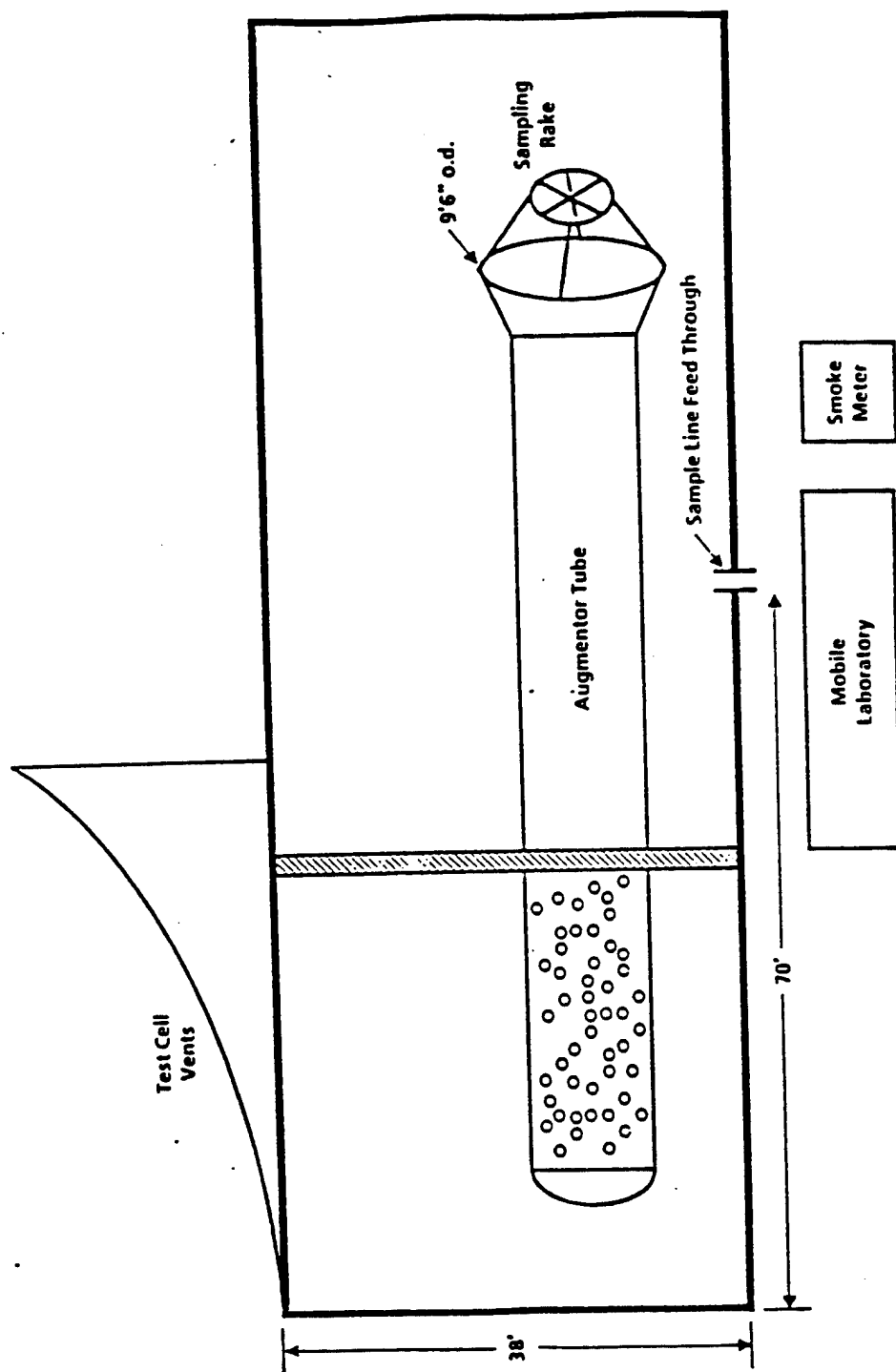


Figure 2. Schematic Diagram of Test Cell (quoted from Reference 1).

TABLE 1. CHARACTERISTICS OF THE EXHAUST OF JET ENGINES IN
A TEST CELL AT FULL POWER (From Reference 1)

	Engine Type		
	J79-17G	TF33-P3	TF33-P7
Thrust, lb	9964	14575	18063
NO, ppm	76.6	68.0	93.0
NO ₂ , ppm	7.4	5.5	2.5
Unburned Hydrocarbon, ppmC	2.2	0.7	1.3
CO, ppm	25	30	15
O ₂ , percent	16.2	16.8	16.2
Exhaust Temperature, °C	609	425	417
Exhaust Flow Rate, lb/sec	167.1	320.2	372.0
Pressure Drop through Exhaust System, psi	1.09	1.59	1.97
Emission Index, lb NO _x /1000 lb fuel	9.0	9.1	10.3
NO _x Emission Rate/lb/hr	74.7	64.1	91.2

scrubber, or other device suffer a pressure drop. This pressure drop can be an important part of the total cost. Fortunately, in a jet engine test cell, the engine has a pumping capacity that is normally wasted. Thus, if the NO_x treatment device requires a pressure drop of 0.2 inches of H_2O , one has the option of replacing that pressure drop by drilling enough additional holes in the end of the augmentor tube to decrease its pressure drop by the required 0.2 inches of H_2O . Of course, the supply is limited. Without regard for the design of the JETC, the maximum total pressure drop the engine can supply is its thrust divided by the cross-sectional area of the augmentor tube; obviously the pressure drop through any NO_x control device needs to be significantly less than this.

The unfavorable implication is that since normal operation of the test cell dilutes the exhaust from the engine before it can be treated, any NO_x control process must operate on a mixture of ambient air and exhaust. Thus the volume of gas that must be treated is increased and the initial NO_x concentration is decreased. While these circumstances are inherently unfavorable to NO_x control, the extent to which they are unfavorable varies from process to process.

While this unfavorable dilution effect can be minimized, it probably cannot be eliminated. For example, the number of holes in the far end of the augmentor tube could be decreased or airflow baffles narrowed. This would increase the system's flow resistance and decrease the amount of ambient air the engine could pump at a given thrust. To get valid test data, however, the engine must be allowed to pump some ambient air. For comparison of one NO_x control process with another, this report assumes satisfactory test cell operation is possible at dilutions of one mole of ambient air per mole of exhaust gas.

C. SCOPE

This report described research done under a DoD phase 1 SBIR program awarded under Contract No. F08635-88-C-0263, "New Technology for Controlling NO_x ." The Introduction of this report discusses the nature of the problem of NO_x emissions from jet engine test cells and explains why presently available or proposed NO_x control technologies are poorly suited for use on jet engine test cells. The experimental methods used in this research are summarized in Section III. Section IV describes the discovery of a new process for controlling NO_x emissions, the BaNO_x process. Section V examines the scientific and engineering implications of the results. The conclusion of this report is that, if the service lifetime of the BaO proves adequate and the quantity of hazardous waste associated with spent catalyst can be tolerated economically, the BaNO_x process is a potential solution to the problem of NO_x emissions from jet engine test cells.

SECTION II

REVIEW OF NO_x CONTROL TECHNOLOGIES

A. CURRENT TECHNOLOGIES

The effort needed to develop a new NO_x control process for jet engine test cells can be justified if it is clear that the presently available NO_x control technologies are not suitable for this application. A number of NO_x control technologies are considered "proven" for one or another kind of application; they have been frequently used with successful results and have well-understood capabilities and limitations. These technologies include 1) a variety of methods of changing the process of combustion to decrease the amount of NO_x produced (*i.e.*, combustion modification technologies) and 2) three methods of removing NO_x from the postcombustion gases: reburning, Thermal DeNO_x and selective catalytic reduction.

1. Combustion Modification

The most commonly used methods of NO_x control are technologies for changing the manner in which the fuel is burned to decrease the amount of NO_x produced during combustion. By definition, these combustion modification procedures are not applicable to engines in a test cell since the purpose of the test is to characterize the engine's unmodified performance.

2. Reburning

The reburning process is exactly what the name indicates. The burned gases coming out of a flame are put through a second flame to reduce the amount of NO_x they contain. To obtain NO_x reduction in this second flame, enough additional fuel must be injected so that the second flame operates under net reducing conditions and at temperatures of 1300°C or greater. While reburning has been successfully applied to coal-fired utility boilers, applying this process to jet engine cells would create severe problems. The amount of fuel needed for reburning would be a factor of eight or more greater than the fuel used by the engine, and temperatures involved in reburning greatly exceed those that could be tolerated inside the augmentor tube.

3. Thermal DeNO_x

In this process, NH₃ is injected into the exhaust gas at temperatures of 700 to 1100 °C and a newly discovered noncatalytic reaction occurs in which NH₃ selectively reduces the NO to nitrogen and water (Reference 2). The reaction time necessary for this novel noncatalytic reaction is quite short, and virtually complete NO reductions can be achieved in only 50

milliseconds. Unfortunately, while Thermal DeNO_x has been quite successful in a variety of near-steady-state applications, it has limitations that make its application to jet engine test cells very doubtful. The present design of test cells require that the hot gases leaving the engine be rapidly mixed with cold ambient air; thus the 50 milliseconds at a temperature greater than 700°C which the Thermal DeNO_x process needs is not readily available. Even if this problem could be overcome there would be significant operating difficulties; *i.e.*, in the Thermal DeNO_x process the amount of NH₃ injected must be continually adjusted to match the concentration of NO in the exhaust gas. In other applications this is not a severe problem since the NO levels varies slowly, but such is not the case for jet engine test cells. Continually adjusting the amount of NO₃ injected would be a significant additional task for the operating personnel. Further, in the Thermal DeNO_x process there is a need to store substantial quantities of ammonia. Since ammonia is a toxic gas, the safety problems involved in storing and using it at a military facility might pose problems.

4. Selective Catalytic Reduction

It is also possible to remove NO_x from an exhaust gas by adding NH₃ to it and passing it through a bed of suitable catalyst at a temperature between 300 and 400°C. Because of this lower operating temperature there are a number of applications in which selective catalytic reduction (SCR) is practical while Thermal DeNO_x is not. Application of SCR to a jet engine test cell, however, would appear to involve severe difficulties.

Catalysts are vulnerable to plugging, fouling, and deactivation. Thus, to avoid damaging the selective reduction catalyst it would probably be necessary to restrict the operation of the engine under test, *i.e.*, avoid operating the engine in a manner that would produce soot, since soot could deactivate the catalyst. As with Thermal DeNO_x there would also be the safety problem of storing large quantities of NH₃. Further, using SCR would greatly increase the difficulties of operating a test cell since (1) the amount of NH₃ injected must be continually adjusted to match the NO level, and (2) the temperature of the exhaust must somehow be adjusted to remain within the 300-400°C operating range of the catalyst.

There is also the cold start problem. A jet engine test cell operates intermittently. When the cell is not in operation, the catalyst can cool toward ambient temperature. The catalyst is a massive object with a large heat capacity, and once it is cooled, it is necessary to pass exhaust gas through it for an extended period until it reaches a temperature at which it can reduce NO_x. During this time (approximately the entire duration typically spent at each power stage) the cell is emitting NO_x to the atmosphere, and this emission can easily exceed the total amount of permitted emissions.

Of all presently available NO_x-control technologies, SCR is by far the most expensive. Application of this technology to a jet engine test cell is likely to be particularly expensive because the amount of catalyst that must be provided is proportional to the maximum

rate at which exhaust gas is produced. This is most unfavorable for systems like jet engine test cells, which must operate intermittently.

B. PROPOSED TECHNOLOGIES

1. RAPRENOX

Perry and Siebers (Reference 3) proposed a new process in which cyanuric acid is injected into exhaust gas at temperatures as low as 400°C and a noncatalytic gas-phase reaction occurs, by which the NO is reduced to molecular nitrogen and water. This reaction was believed to be selective: *i.e.*, it was believed that cyanuric acid could reduce the small amount of NO in exhaust gas. Unfortunately, later work (Reference 4) showed Perry and Siebers's experiments were flawed. The NO_x reduction they observed was not selective: *i.e.*, the amount of cyanuric acid needed corresponded to the very large amount necessary to reduce all of both the NO and O₂. Further, the process was catalytic and subject to all the disadvantages inherent in catalytic treatment of exhaust gas. Other studies (Reference 5) confirm that the low-temperature selective noncatalytic reduction that Perry and Siebers believed they observed is not real. While these studies also showed cyanuric acid could reduce NO at higher temperatures (*i.e.*, temperatures greater than 700°C), the Thermal DeNO_x process can also reduce NO at temperature of 700°C and above. Thus RAPRENOX, to the extent it works at all, does nothing that cannot be done at less expense by Thermal DeNO_x. It is unlikely that the RAPRENOX process will be useful for controlling NO_x emissions from jet engine test cells or in any other application.

2. Electrocatalytic Reduction

R.J. Walker, *et al.*, (Reference 6) of Ceramtec Corporation have proposed a NO_x control process in which the exhaust gas is passed through the cathode section of a solid electrolyte cell. The NO in the exhaust can react at the cathode to form oxide ions which then migrate through the solid electrolyte, a doped zirconia, to the cathode where they form O₂. The nitrogen atoms which are left at the cathode combine to form molecular nitrogen. While this process has been demonstrated on a laboratory scale, in gases which contained NO but not O₂, there is no evidence that the process can remove NO in the presence of large amounts of O₂ (something the process must do to be practical). The electrolytic cells, zirconia sliverplated on one side and platinum plated on the other, are quite expensive devices and the reported rates of NO removal per unit area of cell are low. Thus it seems likely that to provide cells with enough surface area to remove NO_x at the rate it is generated by a combustion system would be prohibitively expensive. Finally, since the cells are made of very thin zirconia they are mechanically fragile. This fragility is also a severe problem since an engine in a test cell produces intense mechanical vibrations.

SECTION III

EXPERIMENTAL METHODOLOGY

A. APPARATUS

The apparatus used in this research to study the kinetics and thermodynamics of the reactions of NO and NO₂ with various solid sorbents was EER's Precision Gas Kinetics Flow System. As shown in Figure 3, this system consists of three subsystems, a system for blending fixed gases, a reactor, and an analytical train.

1. The Gas-Handling System

The blending subsystem consists of a set of Fischer--Porter rotameters, each of which has been calibrated by a wet test meter with nitrogen. Readings from those rotameters that were used to measure the flow of gases other than nitrogen were corrected by the procedure published by the manufacturer. The blending system uses the dilution blending method; *i.e.*, a high-capacity rotameter is used to generate a known flow of nitrogen in an upper flow line and a second high-capacity rotameter is used to generate a known flow of nitrogen in a lower flow line. Rotameters of smaller capacity are used to measure smaller flows of other gases. A set of three-way valves allows adding these smaller flows to either the upper or lower flow line. The upper flow line ends in a back-pressure regulator and a small-capacity rotameter. The small-capacity rotameter takes a measured portion of the flow in the upper line and adds it to the lower line. The back-pressure regulator sends the rest to vent. This system allows one to prepare flowing gas mixtures of several components, the amount of each component being accurately known and readily varied in the range of several percent down to the ppm level.

Once the flowing gas mixture is prepared, it is split; part is vented by another back-pressure regulator, and a portion, measured both by a rotameter and a Matheson Mass Flowmeter, is sent to the reactor. This procedure allows the reaction time to be measured with an accuracy of ± 4 percent and allows the reaction time to be varied while holding the mixture composition constant.

As shown in Figure 3, a three-way valve allowed sending the gas mixture either through the reactor to the analytical train or directly to the analytical train. Switching this three-way valve also had the effect of moving the point at which gage G measured the pressure from directly upstream of the reactor to directly downstream of it, thus providing a measurement of the pressure drop through the reactor.

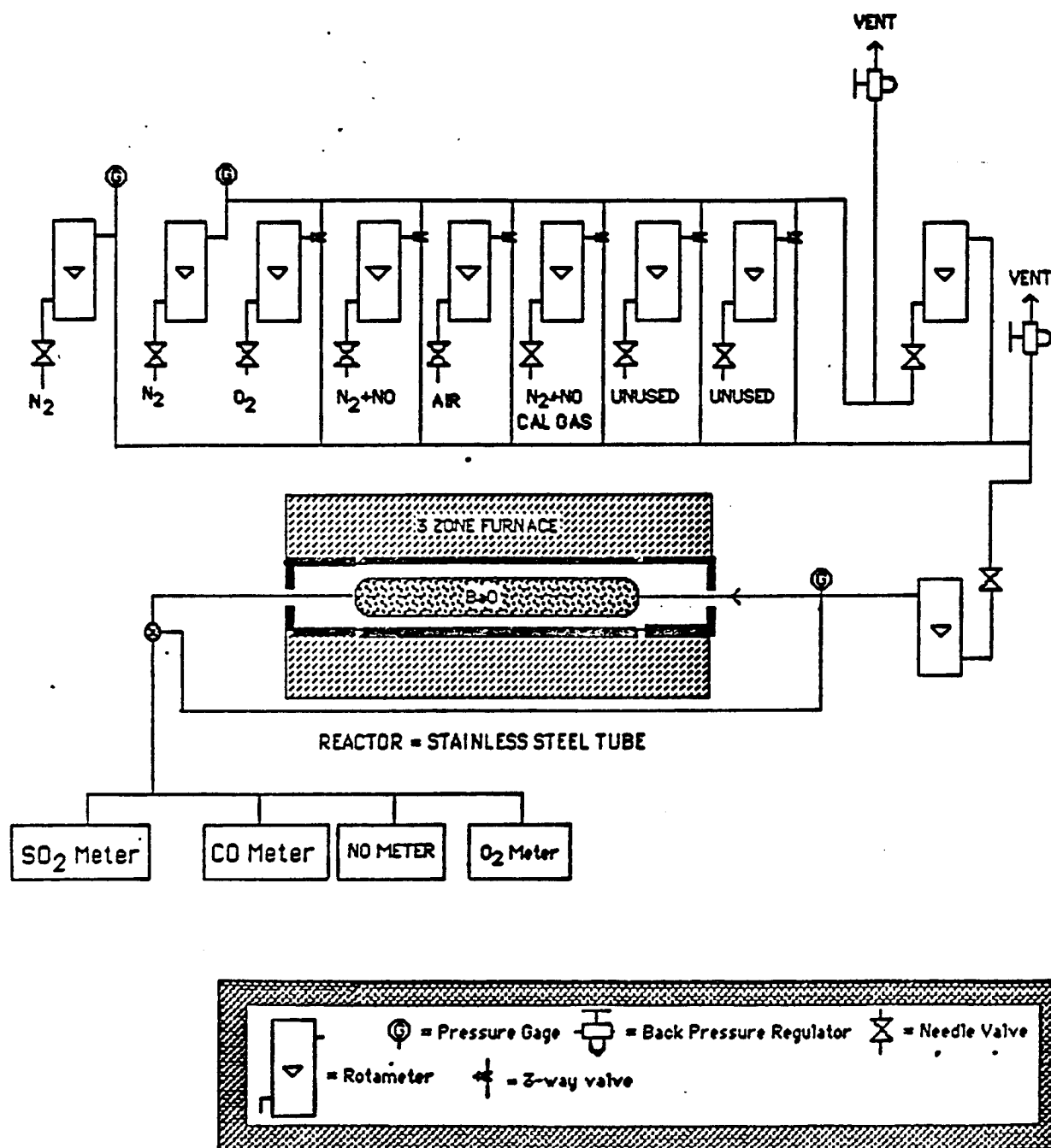


Figure 3. Precision Gas Kinetics Flow System.

The pressure gages on the upper and lower gas blending lines were 1-400 kPa gages from U.S. Gage Co., and the gage on the reactor line was a -20 kPa (vacuum) to 10 kPa gage, also from U.S. Gage Co.

2. The Reactor

The reactor used in most of these experiments is shown in Figure 3. This reactor consisted of an inlet section of 0.635-cm OD x 0.46-cm tubing, a main section of 1.90-cm OD x 1.73-cm ID tubing, and an outlet section of 0.635-cm OD x 0.46-cm ID tubing. This reactor was so placed in a three-zone electric furnace that the main section resided in the portion of the furnace in which the temperature is uniform. Solid NO_x sorbent is confined to the main section of this reactor, of which the volume is 89.3 cm³. Since the volumes of the inlet and outlet sections were only 5 cm³ each, the length of time the flowing gas spends in regions in which the temperature is nonuniform is small compared to the time it spends in the uniform-temperature region. The reactor thus provides an accurately defined contact time between the solid and the flowing gas at an accurately defined temperature.

While this reactor was used in all of these experiments in which kinetic or thermodynamic data were obtained, there were other experiments in which a 1.27-cm OD quartz tube and a 1.27-cm OD ceramic tube were used as reactors.

All gas handling lines were 0.635-cm OD stainless steel tubing or 0.635-cm OD Teflon® tubing.

3. Temperature Control

The three-zone furnace was a Thermcraft tube furnace, 3.18-cm ID, 1-meter total length, with three CA control thermocouples, one in the center of each zone. Signals from these thermocouples went to three Lindberg digital proportional temperature controllers with rate and reset action; *i.e.*, the controllers used a feedback system that sends power to each zone based on the difference between the temperature of the control thermocouple and the set point, the rate at which the control thermocouple temperature is approaching the set point and whether or not there is any long-standing difference between the two.

To monitor the furnace temperature, a set of five CA thermocouples was distributed at equal intervals along the length of the tube furnace. These thermocouples were read by a Doric Digital Thermocouple Reader at a resolution of 1°C. Temperature within the central section of the furnace was uniform to $\pm 3^\circ\text{C}$. In previous experiments in which a traveling thermocouple was used to check the uniformity of the furnace temperature, the temperature in the central section was found to be uniform to better than $\pm 3^\circ\text{C}$.

4. The Instrument Train

Both the gas mixtures going to the reactor and the gas mixture leaving the reactor were sent to a train of gas analysis instruments, which included a Teledyne O₂ analyzer, a Thermoelectron Pulsed Fluorescence SO₂ analyzer, a Thermoelectron Model 48 Gas Filter Correlation CO analyzer, and a Thermoelectron Chemiluminescent NO_x analyzer. While all these instruments were used in a few of our initial experiments, the data in this final report were all obtained with the Thermoelectron Chemiluminescent NO_x analyzer and the Teledyne O₂ analyzer. Both instruments had a precision of better than 2 percent. Thus measurements of the percentage change of NO in a series of experiments were accurate to 2 percent. Both instruments were calibrated daily, the O₂ analyzer with air and the NO meter with a calibration gas mixture purchased from Matheson Gas. Matheson certifies that the analysis they supply with the NO calibration gas is accurate within 2 percent.

The compositions of the flowing gas mixtures calculated from the rotameter settings used to prepare them consistently agreed with the compositions measured by the instruments.

Readings from the NO meter were recorded by a BMC strip chart recorder.

In some experiments the weight gain of samples of BaO experienced on reacting with NO was measured with a Mettler H54 balance.

B. MATERIALS

Gases used in these experiments included N₂ (Matheson ED grade), O₂ (Matheson ED grade), and an N₂ + NO mixture containing 4810 ppm NO, an N₂ + NO mixture containing 51 ppm NO, and an N₂ + NO + NO₂ mixture containing 1770 ppm NO and 170 ppm NO₂. All these gases had a maximum impurity level of 0.1 percent, these impurities being chiefly argon and other gases found in air. Such impurities as CO and hydrocarbons are typically less than 1 ppm.

Granular barium oxide of "commercial grade purity" was purchased from EM Corporation. This material consisted of gray particles with mean diameters in the 1/8- to 1/4-inch range. Pure barium oxide is white and the gray color indicates the presence of impurity carbon left from the manufacturing process (decomposition of BaCO₃ in a reducing atmosphere). While the purity of this material was not high, this was judged to be advantageous. In preparative inorganic chemistry it is often observed that highly purified solids react slowly or not at all under conditions for which materials of commercial purity react readily. No effort was made to characterize this material by X-ray crystallography, but BET surface area measurements on this material showed it to have a surface area of 0.014 m²/g.

Supported barium oxide, *i.e.*, barium oxide dispersed on the surface of a high-surface area support, was prepared by a procedure commonly used for the preparation of high-surface-area catalysts and sorbents (see, for example, Reference 6). In this procedure $\text{Ba}(\text{NO}_3)_2$ was weighed into a glass beaker, and a measured volume of water was added and stirred until the $\text{Ba}(\text{NO}_3)_2$ was completely dissolved. A high-surface-area alumina (surface area greater than $200 \text{ m}^2/\text{g}$) was soaked in this solution for several hours. The excess liquid was then poured off, and the solid dried for several hours in an open steel pan on a hot plate. The dried solid was then loaded into a stainless steel reactor, placed within the three-zone furnace and heated to 1000°C overnight to calcine it. This heating was done under a measured flow of nitrogen so the amount of NO produced during the calcination could be measured. From this measurement it is calculated that this BaO-impregnated alumina contained 2 wt-percent BaO.

Granular calcium oxide was prepared by calcining CaCO_3 (marble chips) at 800° overnight under flowing nitrogen.

Other materials tested included NaHCO_3 , NaHSO_3 , and two kinds of lime (Linwood calcite hydrate and Colton). Detailed results for these materials will not be reported because all four sorbents showed only trivial ability to remove NO from combustion effluents. While all four showed some ability to remove NO_2 , this was a relatively slow process in all cases.

C. EXPERIMENTAL PROCEDURE

The following procedure was used in all experiments reported below. The NO and O_2 meters were calibrated, the furnace was turned on and allowed to heat until a steady temperature was achieved, and the flows of gases through the rotameters were initiated and adjusted to the desired values. At the start of each run, the flow of gases produced by the gas-blending system was sent directly to analysis to determine the initial NO and NO_2 concentrations. The gas mixture was then passed through the reactor and the change in NO or NO and NO_2 concentrations was determined for the conditions of interest. During this procedure rotameter readings were frequently checked to verify that they were maintaining their initial values, and the gas mixture was frequently sent directly to analysis to establish that the present composition was the same as the initial composition.

SECTION IV

RESULTS

A. THE BaNO_x REACTION

Early in this research it was found that BaO had remarkable ability to capture both NO and NO_2 from simulated exhaust gas. Figure 4 shows the results of the first set of experiments in which this surprising reaction was observed.

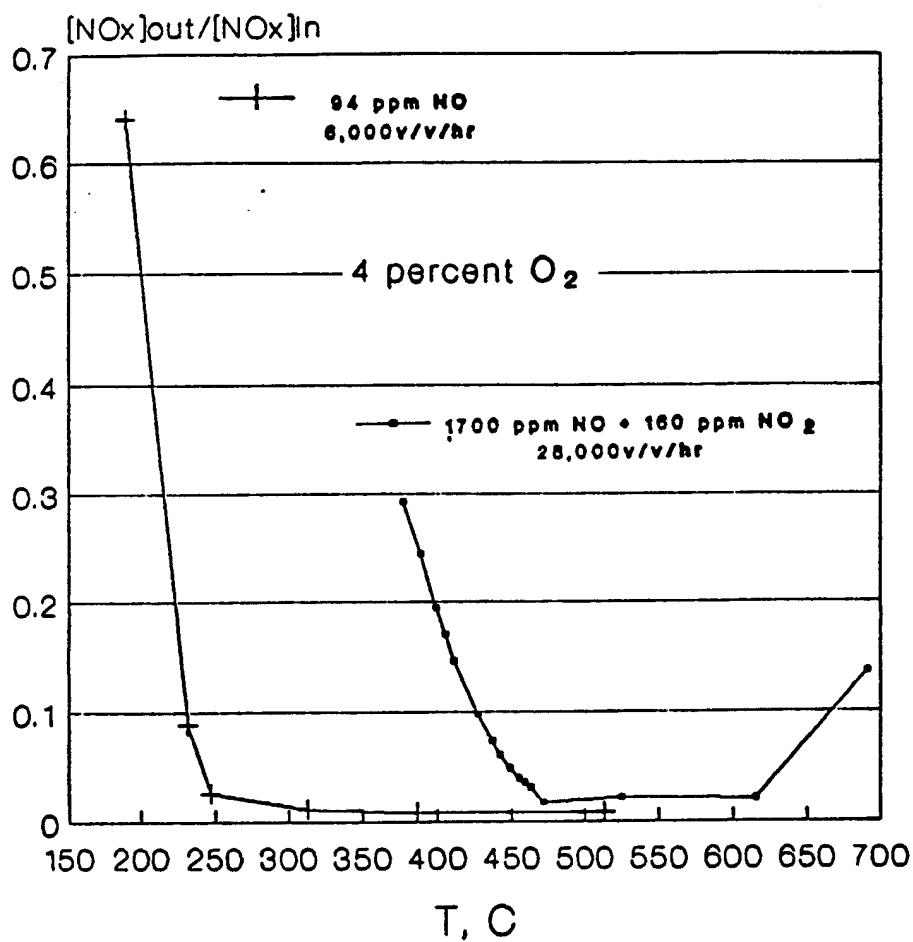


Figure 4. NO_x Capture by a Bed of BaO .

B. THERMODYNAMICS OF THE BaNO_x REACTION

A sample of barium oxide was partially reacted with NO and experiments were then done in which a gas mixture containing variable amounts of NO was passed over the sample. It was found that there was a critical NO level such that mixtures containing more NO than this level experienced a decrease in NO content, whereas the NO content of mixtures containing less than this level increased.

This critical level is believed to represent the equilibrium pressure of NO in its reaction with barium oxide. As shown in Figures 5 and 6, the equilibrium pressure of NO in this reaction depends on both the temperature and the amount of O_2 present. This implies that the reaction between NO and barium oxide also involves oxygen and that one molecule of O_2 is consumed for every two molecules of NO. From Figure 5 one can use the Clausius-Clapeyron equation (Reference 7) to calculate that ΔH for the reaction between BaO , O_2 , and NO is 39.5 kcal/mole of NO.

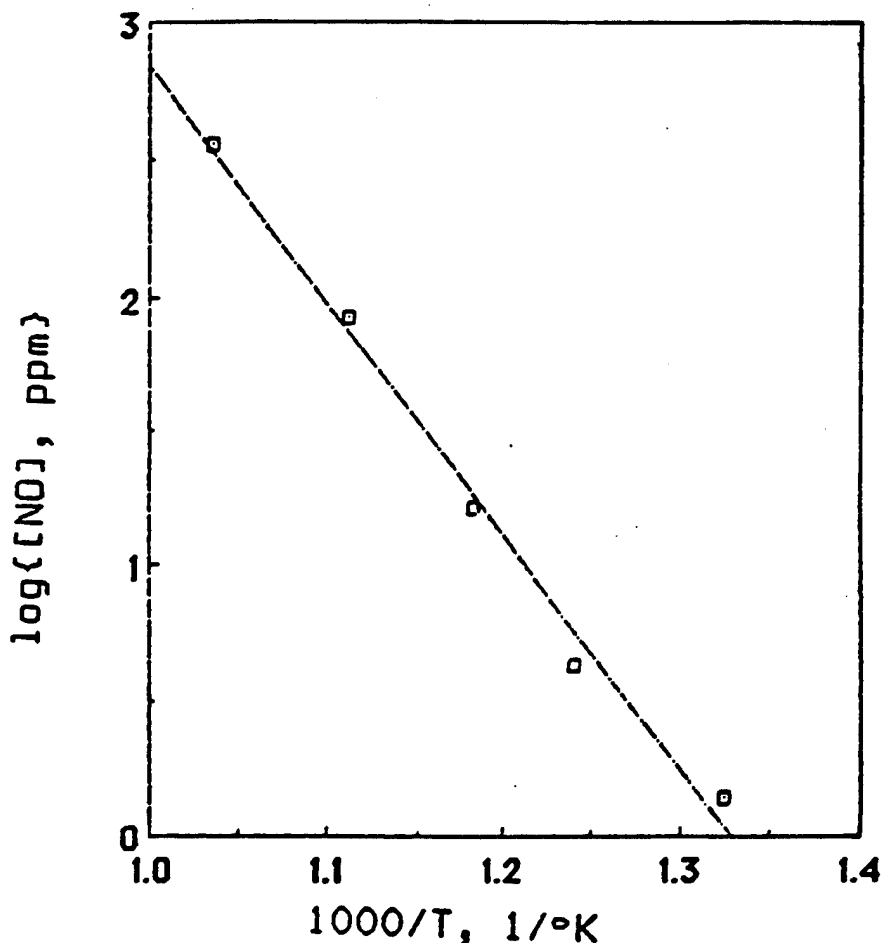


Figure 5. Temperature-Dependence of the Equilibrium Pressure of NO.

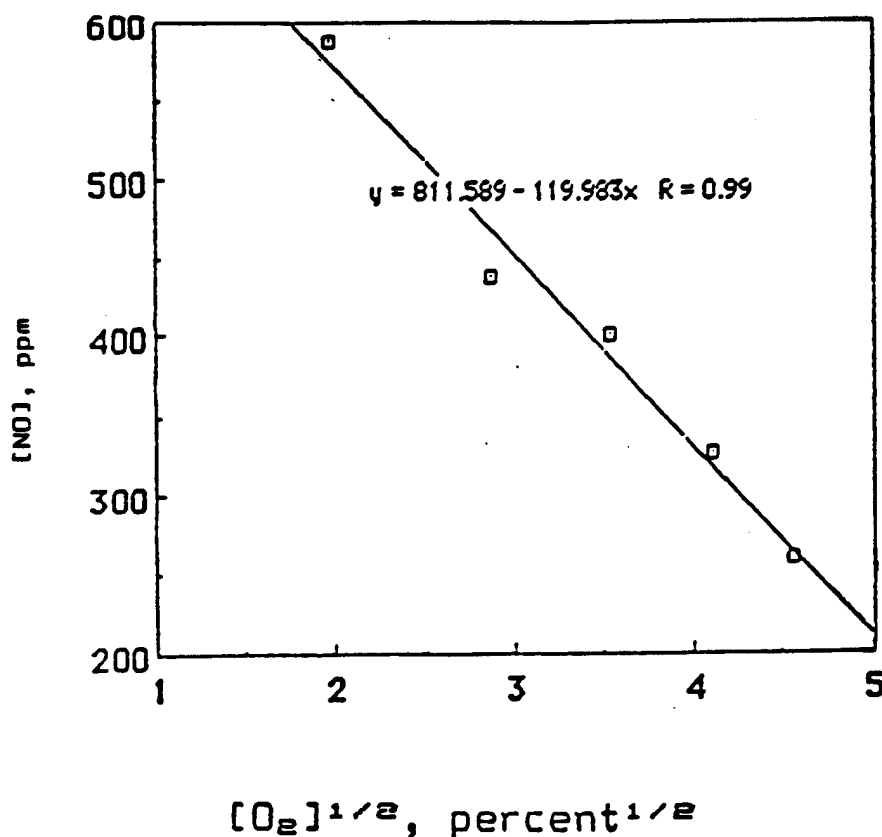
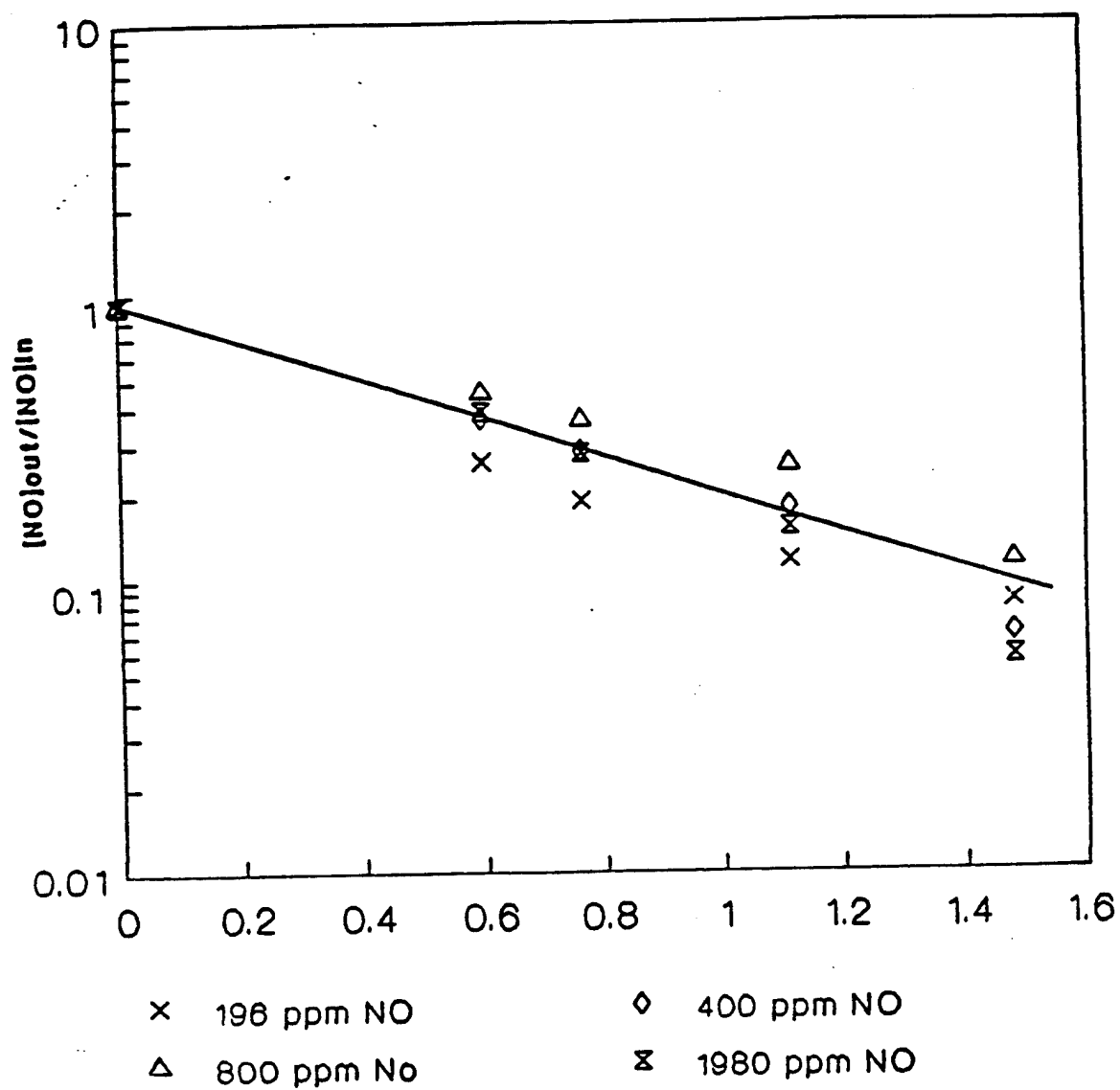


Figure 6. Oxygen-Dependence of the Equilibrium Pressure of NO.

C. THE KINETICS OF THE $BaNO_x$ REACTION

To determine the kinetics of the reaction between NO and barium oxide, experiments were done in which gas mixtures containing NO and O_2 were passed over barium oxide and the amount of NO removed was measured as a function of the contacting time. If the rate at which NO is removed from the gas phase is proportional to the amount of NO in the gas phase, one would expect the log of the fraction of the initial NO remaining plotted against the contacting time to be a straight line. (Plots of this kind are called first-order rate plots.) Figure 7 shows a set of such plots for initial NO concentrations ranging from 198 to 1980 ppm, all done at 279°C and 4.8 percent O_2 . Since the points at all four initial NO levels fall on or close to the same straight line, the rate of NO removal by the barium oxide is proportional to the concentration of NO.



$[NO]_{in}$ = 196, 400, 800, and 1980 ppm
 279°C, 4.8 percent O_2

Figure 7. First-Order Rate Plots for the
 NO + BaO Reaction.

Figure 8 shows a first-order rate plot for a set of experiments in which the amount of NO remaining was measured as a function of contact time for three different concentrations of O_2 . Since all the points show a good fit to the same straight line, the rate of NO removal by barium oxide is independent of O_2 .

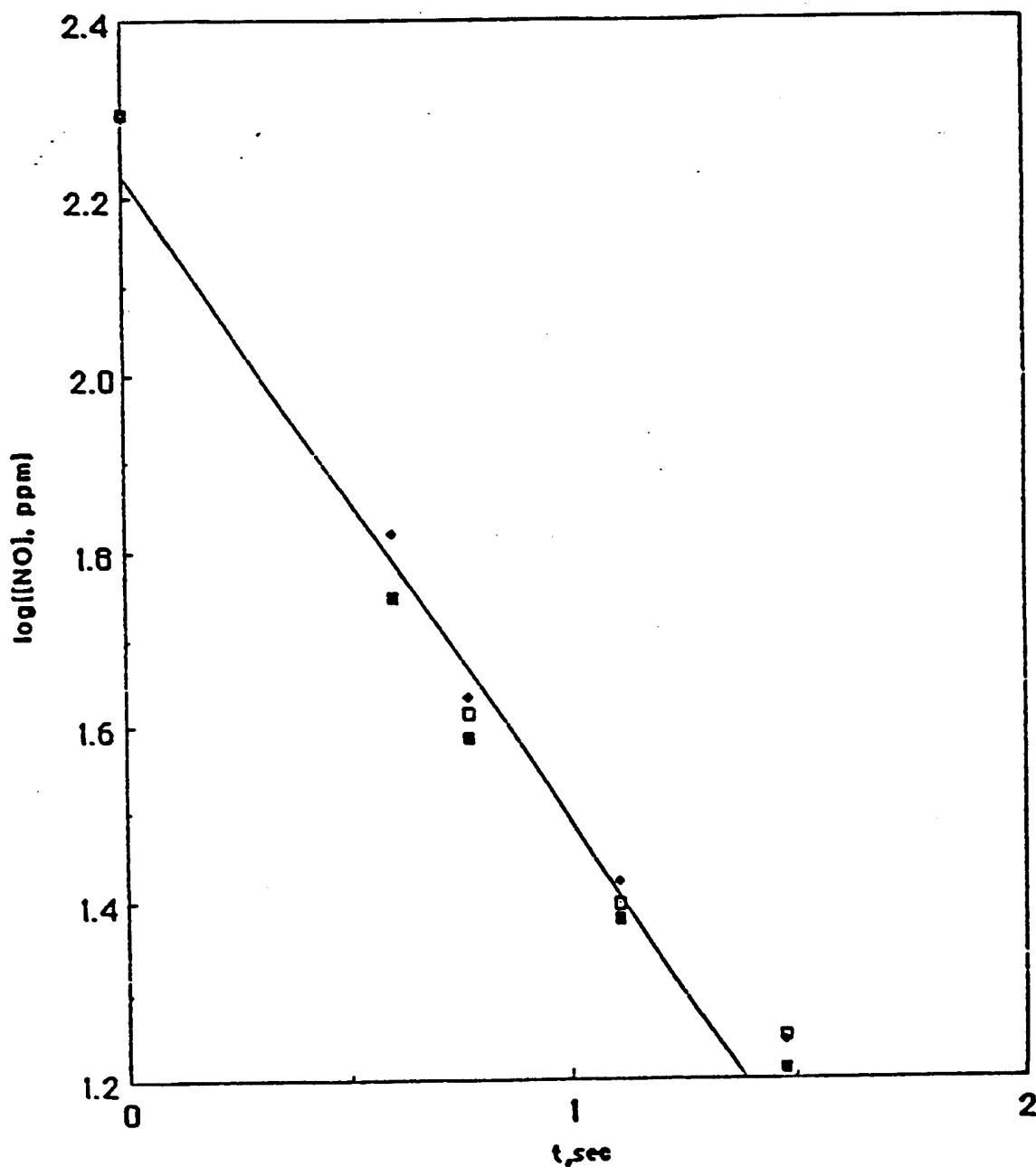


Figure 8. First-Order Rate Plot for Removal of NO by BaO at 279°C and 4.8, 3.0 and 1.1% O_2 , \diamond , \square , and \blacksquare , Respectively.

Figure 9 shows first-order rate plots for NO removal at various temperatures. These data indicate an activation energy for the process of 12.7 kcal/mole.

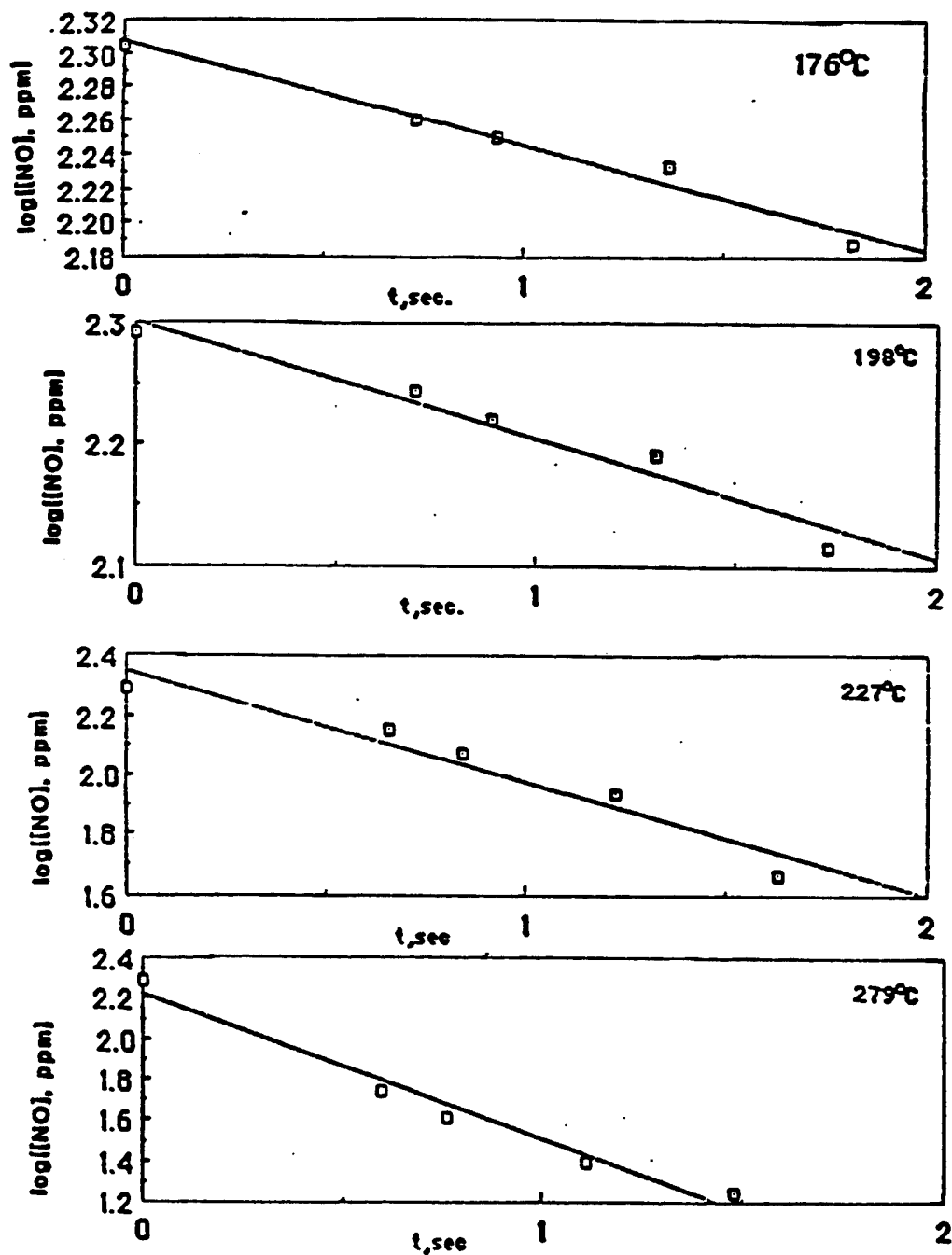


Figure 9. First-Order Rate Plots for Removal of NO by BaO at Various Initial Temperatures.

D. DEVELOPMENT OF A GENERAL RATE LAW

The two sets of experiments reported above define the BaNO_x reaction under two sets of limiting conditions: temperatures so low and contact times so short that the kinetics is controlling and temperatures so high and contact times so long that thermodynamic equilibrium is controlling. Practical use of the BaNO_x reaction is likely to involve conditions for which both kinetics and thermodynamics are important but not controlling; it is therefore desirable to develop a general rate law that accounts for both factors.

Such a general rate law may be developed based on the following argument: the rate at which barium oxide containing some captured NO captures more NO from the gas phase would be proportional to both its surface area, S , and to $[\text{NO}]$, the concentration of NO in the gas phase. The rate at which it releases captured NO to the gas phase will be proportional to S . Thus, one would expect the rate law to be

$$d[\text{NO}]/dt = k_d S - k_c S [\text{NO}]$$

in which k_d and k_c are the rate constants for release and capture of NO, respectively. If the reaction comes to equilibrium then $d[\text{NO}]/dt = 0$, and the equilibrium concentration of NO, $[\text{NO}]_{\text{eq}}$, is given by the equation

$$[\text{NO}]_{\text{eq}} = k_d/k_c$$

From this it can readily be shown that

$$d([\text{NO}] - [\text{NO}]_{\text{eq}})/dt = -k_c S ([\text{NO}] - [\text{NO}]_{\text{eq}})$$

which may be rewritten as

$$d(\ln([\text{NO}] - [\text{NO}]_{\text{eq}}))/dt = -k_c S$$

Thus, under conditions for which both kinetics and thermodynamics are important, one expects that the reaction will be first order in $[\text{NO}] - [\text{NO}]_{\text{eq}}$ rather than in $[\text{NO}]$. The data in Table 2 confirm this expectation and Figure 10 shows an Arrhenius plot, using the rate law derived above, for the temperature range 176°C to 692°C. Thus a general rate law for the BaNO_x reaction is available.

TABLE 2. REACTION RATE DATA AT CONDITIONS FOR WHICH BOTH KINETICS AND THERMODYNAMICS ARE IMPORTANT.

T = 627.4°C, t = 0.333 sec.,				
[NO] _{eq} = 85 ppm				
[NO] _{IN} = 275 ppm	225 ppm	175 ppm	133 ppm	
[NO] _{OUT} = 125 ppm	115 ppm	106 ppm	95 ppm	
$\frac{[NO]_{OUT} - [NO]_{eq}}{[NO]_{IN} - [NO]_{eq}} = 0.211 \quad 0.214 \quad 0.233 \quad 0.208$				
Ave. = 0.217 ± 0.004				
T = 573°C, t = 0.350 sec.,				
[NO] _{eq} = 16.3 ppm				
[NO] _{IN} = 68 ppm	38 ppm	23 ppm		
[NO] _{OUT} = 28 ppm	20 ppm	18 ppm		
$\frac{[NO]_{OUT} - [NO]_{eq}}{[NO]_{IN} - [NO]_{eq}} = 0.226 \quad 0.234 \quad 0.254$				
Ave. = 0.238 ± 0.011				
T = 533.4°C, t = 0.367 sec.,				
[NO] _{eq} = 4.3 ppm				
[NO] _{IN} = 14.5 ppm	7.8 ppm	5.2 ppm		
[NO] _{OUT} = 6.5 ppm	5.0 ppm	4.5 ppm		
$\frac{[NO]_{OUT} - [NO]_{eq}}{[NO]_{IN} - [NO]_{eq}} = 0.216 \quad 0.20 \quad 0.22$				
Ave. = 0.212 ± 0.008				

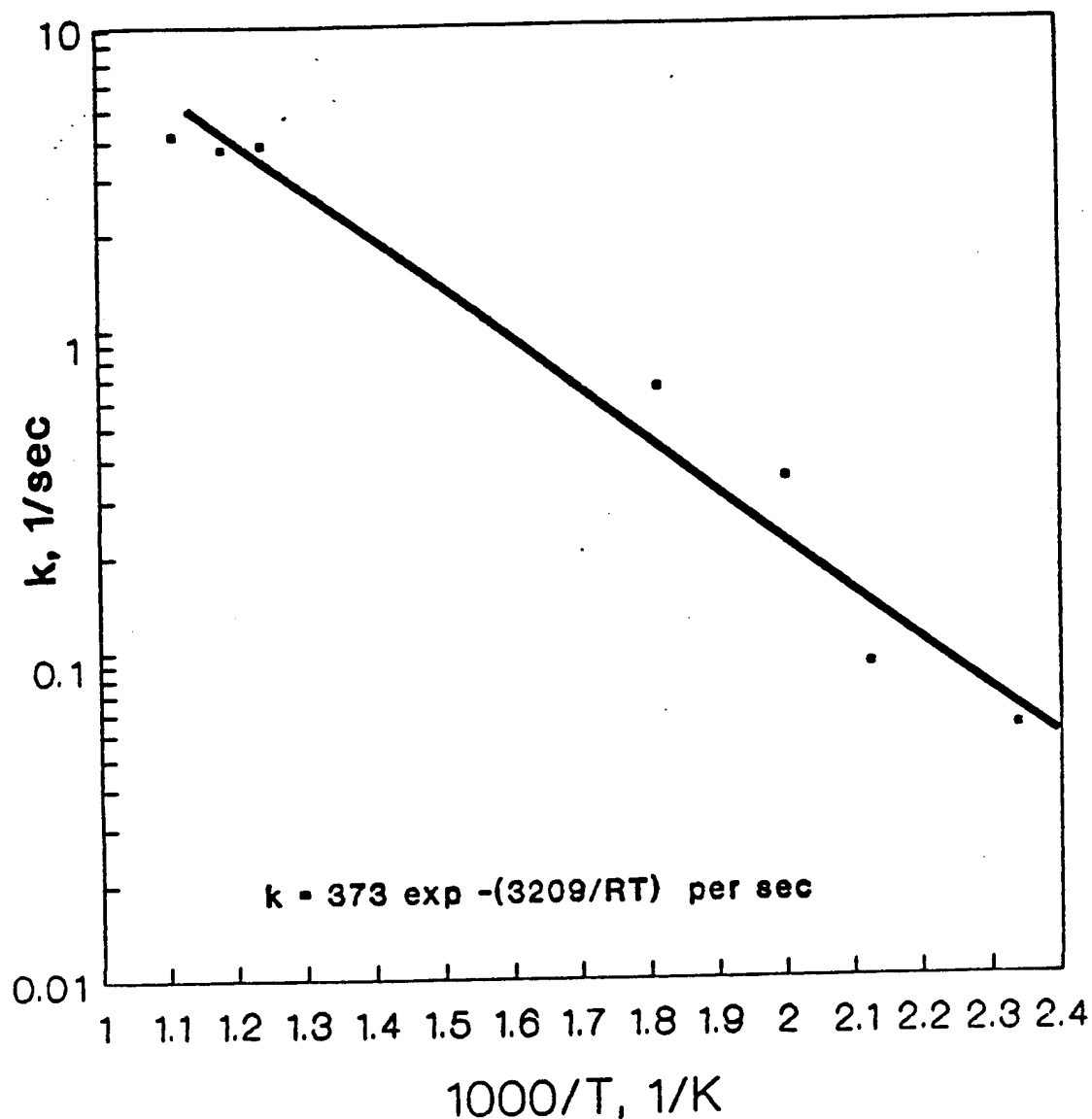


Figure 10. Arrhenius Plot for the NO + BaO Reaction.

E. PRESSURE DROP

During the course of the experiments reported above, the pressure drop of the gases flowing through the reactor was monitored. At the highest flow rates used it was 2 kPa or less (2 kPa = 0.29 psi). As the pressure drop through the reactor was less than 2 percent of the total pressure, the ambiguity it causes in the contacting time and, hence, the possible error it introduces into the measured rate constant for NO adsorption is less than 2 percent.

F. PRODUCT IDENTIFICATION

It is imaginable that the reaction between barium oxide, NO, and O₂ could yield either Ba(NO₃)₂ or Ba(NO₂)₂, though the former is more stable thermodynamically and, hence, more likely. To decide this issue, tests were done with Merckquant® Nitrite and Nitrate Test Strips (Reference 8), which indicate the presence of nitrate and/or nitrite ions by the reaction of nitrous acid with an aromatic amine, which then undergoes a coupling reaction to form a red-violet azo dye. A solution of the product of the BaO + NO + O₂ reaction was prepared and tested. The nitrite test strip showed no color formation, while the nitrate test strip immediately demonstrated strong color. Sulfamic acid was added to the reaction product solution to suppress possible interfering reactions and the nitrate test repeated. Since the result was again positive, the reaction product is a nitrate salt. Thus since the starting material was a barium compound, the cation in this salt is barium and the salt is barium nitrate.

As a matter of thermodynamics, the reaction among BaO, NO, and O₂ could also produce NO₂. During the experiments reported above the Chemiluminescent NO_x meter was frequently switched from its NO_x mode to its NO mode. During experiments in which NO-containing gas mixtures were passed over barium oxide, no difference between these modes was ever observed, implying that none of the NO that escaped capture was converted into NO₂. Similarly, when barium oxide that had captured some NO was decomposed, no NO₂ was observed. One might, however, worry that NO₂ could be present in the gases escaping the barium oxide and still not be observed because the stainless steel reactor had converted it into NO before analysis.

To eliminate this worry, a brief set of experiments was done in which barium oxide that contained some NO was decomposed in a ceramic tube. No NO₂ was observed.

G. NO CAPACITY

In one experiment a piece of barium oxide was heated overnight at 450°C under a flowing gas mixture containing N₂, O₂, and NO, after which the increase in the weight of the piece was determined. A 23.5 percent weight increase was found. This corresponds to converting 33 percent of the initial BaO into Ba(NO₃)₂.

H. SUPPORTED BaO

Toward the end of this research, a very brief series of experiments was done with barium oxide supported on high-surface-area alumina. Figure 11 compares the results of these experiments with previous experiments with granular barium oxide.

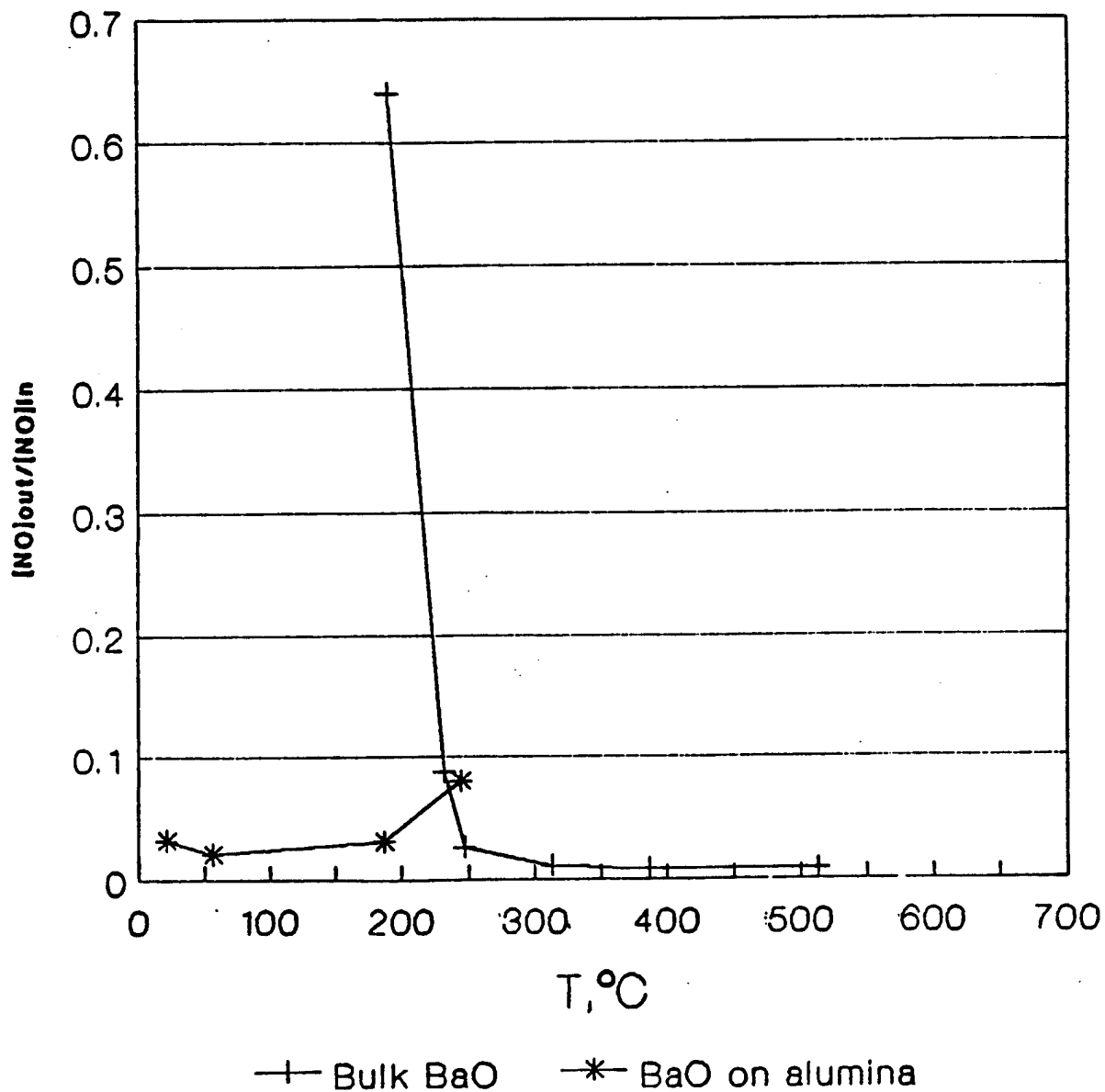
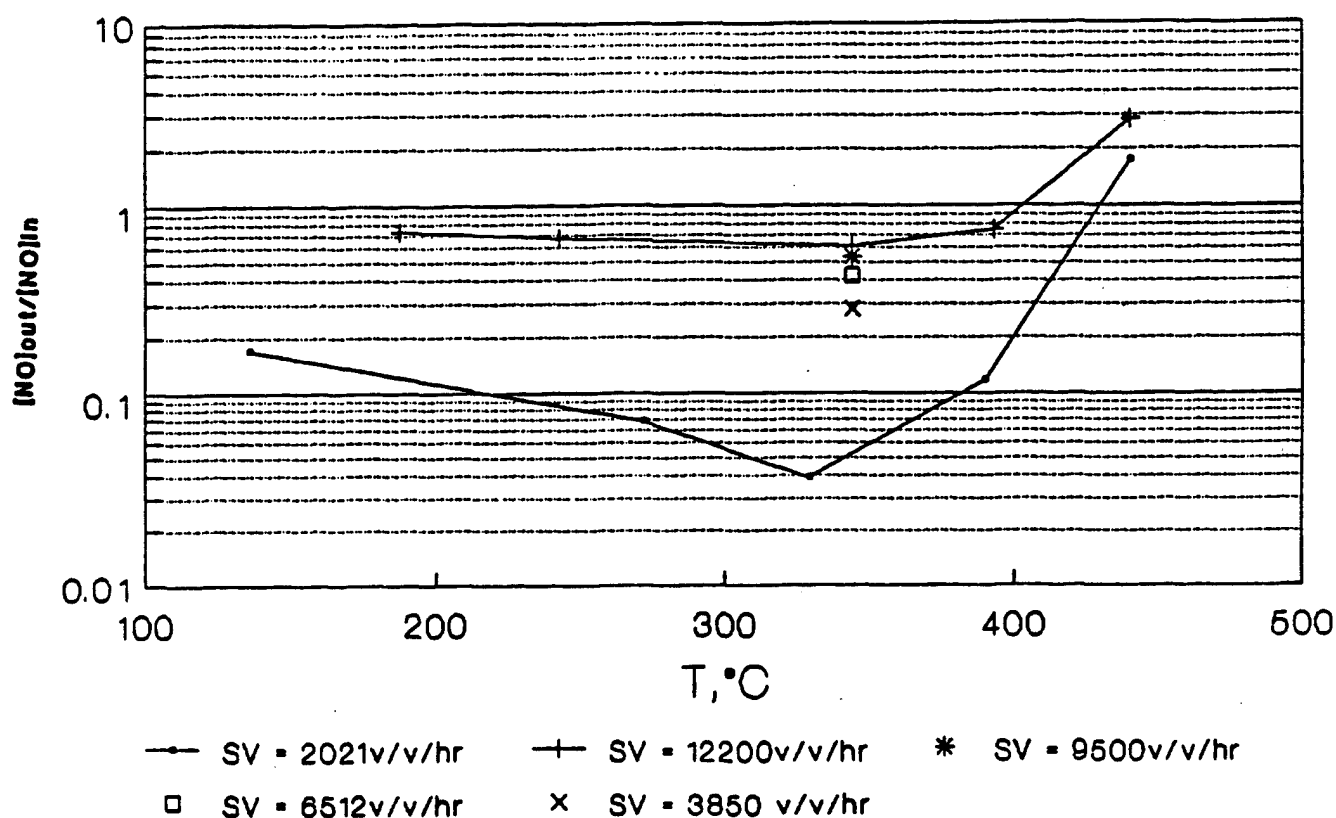


Figure 11. Comparison of NO Capture by Supported and Granular BaO.

I. GRANULAR CaO

Results of another brief set of experiments done with granular calcium oxide are shown in Figure 12. The data in Figure 12 were obtained at an O_2 level of 15.4 percent. While quantitative data were not obtained at lower oxygen concentrations, it was observed that the capture of NO decreased rapidly with decreasing O_2 concentrations.



Input NO = 220 ppm, O_2 = 15.4 percent

Figure 12. Capture of NO by CaO.

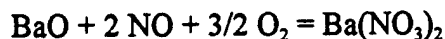
SECTION V

DISCUSSION

A. SCIENTIFIC IMPLICATIONS OF THE RESULTS

1. Thermodynamics of NO Capture by BaO

The product identifications given above are consistent with the reaction



The thermodynamic equilibrium data, however, imply that the stoichiometry of the reaction is one O_2 for every two NO molecules. The explanation for this seeming contradiction is that the reaction occurs in stages:



If the former reaction is slow on the time scale of our experiments while the latter is fast, the observed equilibrium would correspond to the second reaction and would show the observed half-order dependence on oxygen.

The assumption that the observed equilibrium is reaction (2) is also consistent with the observed heat of the reaction. From the data in Reference 9, ΔH for reaction (2) is -37.6 kcal/mole of NO, in good agreement with our experimental value of -39.5 kcal/mole of NO.

Support for the two-step mechanism suggested above can be found in the literature. Moeller (Reference 10) reports that the first step of this mechanism, reaction of barium oxide with molecular oxygen to form barium peroxide, occurs readily. Reference 11 reports qualitative data showing that NO reacts readily with barium peroxide in the presence of oxygen.

2. Kinetics of NO Capture by BaO

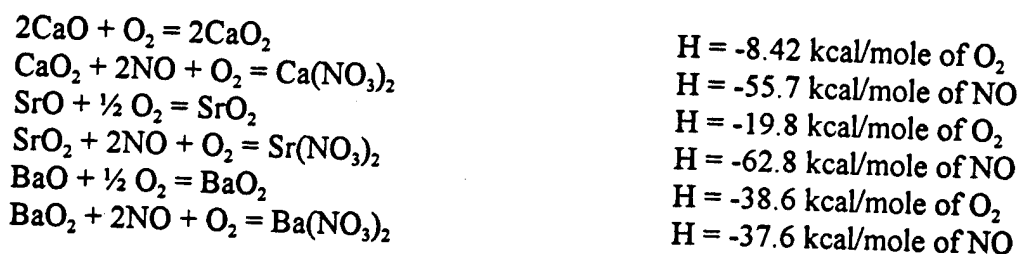
The factors that determine the rate of a chemical reaction are quite different from those that determine the thermodynamics. While the initial and final states of a system determine the thermodynamics, the path determines the kinetics. Often one step will be the slowest and will determine the overall rate. In this study the thermodynamic equilibrium was observed to depend

on the half power of the oxygen concentration whereas the rate of the reaction was found to be independent of the oxygen concentration.

One possible explanation for this observation is that the rate-determining step is a reaction between NO and peroxide ions to form intermediates, which subsequently react with oxygen and ultimately form nitrate ions.

3. Capture of NO by CaO and by SrO

While the reaction mechanism discussed above can also occur with CaO and SrO, these reactions (Reference 9) are thermodynamically different from those of BaO. Thus,



What these thermodynamic data show is that the peroxides of all three alkaline earth metals should be capable of rapidly capturing NO to form the nitrate. Barium, however, is unique in that its oxide readily reacts with air to form the peroxide. Strontium oxide will react with molecular oxygen to form the peroxide only under forcing conditions. Even under forcing conditions calcium oxide will not react with molecular oxygen to form the peroxide except to a very minor extent, *i.e.*, conversion of the surface of the oxide particles into the peroxide. Calcium oxide can, however, be converted into calcium peroxide by reaction with hydrogen peroxide.

Given the above, one might speculate that, like barium oxide, calcium oxide would capture NO to form the nitrate but that, because of the greater difficulty of forming the intermediate peroxide, the calcium reaction will be much slower.

The data in Figure 12 are consistent with this expectation.

One might also expect that the rate of capture of NO by strontium oxide would be intermediate between that of barium and calcium oxides and that the peroxides of both strontium and calcium would be capable of very rapid NO capture. There is some support in the literature for this speculation. Reference 12 reports experiments in which MgO_2 , CaO_2 , and BaO_2 were contacted with NO. Specifically, Figure 13 from that reference shows data for a set of experiments in which a simulated flue gas containing 10 ppm NO was passed through 10 grams of calcium peroxide at 25°C at a flow rate of 300 cm³/min. While the reference provides no further

information on conditions, a typical packed bed will have a density of roughly 50 percent of the theoretical density of the packing material. Thus for the experiment in which a 10-g bed of CaO_2 was used, a 300 $\text{-cm}^3/\text{min}$ flow rate would correspond to a space velocity of 2600 v/v/hr . Since

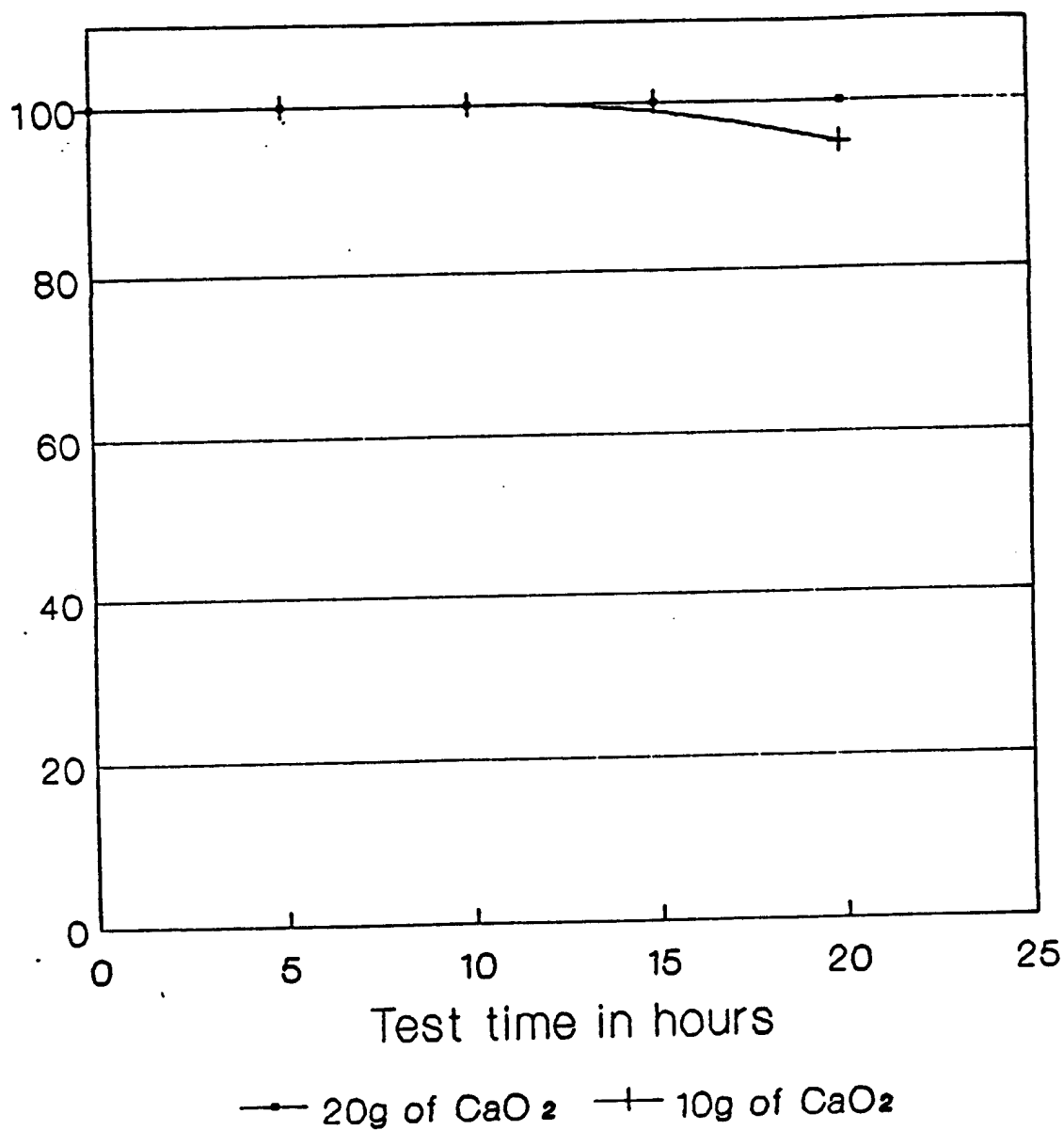


Figure 13. Capture of NO by CaO_2 , 25°C, 50 Percent Relative Humidity, 10 ppm NO, Data from Reference 12.

Figure 13 shows 100 percent capture of the NO at an operating temperature of only 25°C, it is evident that calcium peroxide is significantly more effective for removing NO than is calcium oxide or barium oxide.

4. Supported BaO

If the rate at which barium captures NO from exhaust gas is proportional to the surface area of the barium oxide, then one would expect that increasing the surface area of the barium oxide by spreading it out over a high-surface-area support would increase the rate of NO capture. The data in Figure 11 confirm this expectation. Thus, for example, Figure 11 shows an NO capture of 96.8 percent at 21°C and a space velocity of 2021 v/v/hr. This corresponds to a rate constant for NO capture of 1.93 sec⁻¹. In contrast to this high value, Figure 11, an Arrhenius plot for the capture of NO by bulk BaO, gives an extrapolated value for the capture rate constant at 21°C of only 0.00119 sec⁻¹. Thus, supporting the barium oxide on high-surface-area alumina increases its reactivity by a factor of 1600.

B. ENGINEERING IMPLICATIONS OF THE RESULTS

1. The Ideal Technology

One way to place the results of this study in perspective is to imagine an ideal process for controlling NO_x from jet engine test cells and compare a NO_x-control process based on these results with this ideal.

a. Noninterference

Probably the most important aspect of such an ideal solution is noninterference. A jet engine test cell is a complex testing facility, and operating it is a highly demanding task. The last thing one wants is a NO_x-control technology that demands substantial time and attention from the operating personnel and thus distracts them from their normal tasks. If one were free to wish for the perfect NO_x-control technology for jet engine test cells one would wish for an ideal device which could be put on the back end of the test cell. NO_x-containing gases go into this ideal device, pure gases flow out of it. This device would not need service if it was completely ideal. If it was very nearly ideal it would need service only infrequently and that service would be something that a contractor could provide at modest cost.

b. The Ability to Retrofit

The other very important aspect of an ideal solution is its ability to retrofit: the ideal device has to work under the conditions provided by the existing test cell. That translates into a number of specific requirements.

c. Resistance to Flow

In many NO_x -control technologies, the pressure drop the exhaust gas suffers going through the control device is a significant cost. A NO_x -control system for jet engine test cells would, however, avoid this cost if the pressure drop through the control device were significantly less than the thrust of the engine divided by the area of the augmentor tube.

d. Selectivity for NO over O_2

The exhaust from a jet engine will typically contain more than 1000 times as much O_2 as NO. Any practical NO_x -control system, therefore, must be selective, *i.e.*, it must act only on the NO while not affecting the much larger amount of O_2 .

e. Temperature

Since jet engine test cells are operated intermittently it's to be expected that, at the start of any test, the control device will have cooled to ambient temperature. It would probably be unacceptable for the test cell to emit NO_x while the control device is warming up and therefore the control device should be able to remove NO_x when it is at or close to ambient.

As the test proceeds, the temperature of the ideal device will increase, eventually approaching that of the diluted exhaust gases passing through it. This temperature will depend on the initial temperature of the exhaust, the amount of ambient air it mixes with, and the amount of heat lost before reaching the control device. While this is a complex situation it is probably desirable for the ideal device to be able to operate at temperatures up to at least 300°C .

f. Space Velocity

The control device also needs to be small enough to fit in the available space. However, the smaller the control device is, the more rapidly the exhaust gas will pass through it. Thus, the need to keep the control device size down to reasonable dimensions implies a requirement defining the speed with which the control device must remove NO.

A numerical example makes this clearer. The test cell shown in Figures 1 and 2 has a rear section that is 33 feet long and 30 feet wide. Assuming that a control device 33 feet long by 30 feet wide by 30.3 feet tall is placed on top of this rear section, and that the engine operates at full power, producing exhaust at 372 lb/sec and 417°C , this exhaust being diluted with 372 lb/sec of 25°C ambient air, with the exhaust ambient air mixture having a temperature of 221°C , one can readily calculate that the gases will pass through the control device in only 1.79 seconds.

In the study of catalysis and related subjects it is the custom to express residence time in terms of its inverse, which is called the space velocity. Space velocity is defined as being the volume of gas passing through a reactor per unit volume of the reactor per hour. Thus the residence time of 1.79 seconds (or 0.000497 hr) corresponds to a space velocity of 2010 v/v/hr.

Of course, this example would change if other numbers were assumed, but it still seems likely that if the control device is to fit comfortably into the space available in a test cell, it must operate at a space velocity of at least 2000 v/v/hr.

g. Capacity

The control device also needs to have a reasonable capacity for NO so the interval between recharge it is not unduly short.

h. Disposability of Waste Products

An ideal NO_x control technology either would not produce any waste products or would produce only small amounts of nonhazardous waste products that are readily disposed of.

2. Comparison with the Requirements of an Ideal Process

From the experimental results given above it would appear that barium oxide meets or approaches all these requirements for an ideal NO_x control technology.

a. Space Velocity

Since all the experiments reported herewith involved space velocities in excess of 2000 v/v/hr this requirement is fully met.

b. Resistance to Flow

For the sake of an example, assume that the 33-foot x 30-foot x 30.3-foot control device discussed above is filled with panel beds of BaO, these beds having a thickness of one foot. In Table 1, a group of typical engines at full power develop enough thrust that the pressure drop through the exhaust system is in the range of 1.09 to 1.97 psi for 30 to 54 inches of water, most of this drop occurring as the exhaust gas passes through the set of holes in the rear of the augmentor tube. In the experiments in this report, the pressure drop passing through a 1-foot-long reactor filled with granular BaO was 0.29 psi at the highest flow rates tested. Thus, for

panel beds with a thickness of 1 foot, the pressure drop needed to pass the exhaust through a bed of BaO is readily available.

c. Selectivity for NO over O₂

The removal of NO with BaO is highly selective, removing only stoichiometric quantities of O₂.

d. Temperature

While the bulk BaO is not effective for NO capture at ambient temperature, supported BaO is. Thus the temperature requirement may be met by using a bed consisting of 20 or 30 weight percent supported BaO and balance bulk BaO.

e. Capacity

A bed of BaO of the size discussed above (30 feet x 33 feet x 30.3 feet) will, if packed at 1/5 of theoretical density, hold 13,940 pound-moles of BaO. Assuming that this bed can capture NO_x to 1/3 of its stoichiometric capacity, that corresponds to 427,000 pounds of NO_x, which, at 91.2 lb/hr of full-power operation during 500 hours of full power/year, would allow the bed to clean the test cells exhaust for 9.37 years between rechargings.

If, instead of bulk BaO, supported BaO (3 wt.percent BaO) were used, this interval would drop to 3.4 months.

f. Disposability of Waste Products

In this regard BaO is less than ideal since it is a toxic substance. While BaO is readily converted to BaSO₄, precautions are still required in disposal, as BaSO₄ is considered a hazardous air pollutant.

3. Possible Problems

Given the above encouraging analysis, there are still a number of possible problems which have not been addressed in this research.

a. Mechanical Strength of the BaO

A bed of BaO on the back end of a test cell would be subject to the intense sound waves that the jet engine generates. This might lead to mechanical disintegration of the BaO particles. If the fine particles thus generated stayed within the bed, its resistance to flow

could increase beyond acceptable limits. Additionally, exhausting of such fine particles could produce unacceptable particulate emission levels.

While this might be a problem for using bulk BaO it seems most unlikely to be a problem for BaO supported on high-surface-area alumina. The latter is an extremely strong material widely used in the chemical industry because of its extraordinary resistance to abrasion.

b. Reaction of BaO with CO₂

While the kinetics of the reaction of BaO + CO₂ → BaCO₃ is unknown, the process is thermodynamically quite favorable. Exhaust gas, of course, contains both CO₂ and NO and one might worry that the BaO might react with both and that this reaction with the much larger amount of CO₂ present could greatly decrease the BaO bed's capacity to remove NO.

This, however, is not nearly as severe a problem as it might appear. If the BaO + CO₂ → BaCO₃ reaction is slow relative to the BaO + NO + 3/2 O₂ → Ba(NO₃)₂ reaction it will not be a problem. If its rate is comparable or faster, then the thermodynamic principle that "systems in equilibrium with the same system must be in equilibrium with each other" comes into play. This principle implies that if both the BaO + CO₂ → BaCO₃ and the BaO + NO + 3/2 O₂ → Ba(NO₃)₂ reactions are facile processes the BaCO₃ + NO + 3/2 O₂ = Ba(NO₃)₂ + CO₂ reaction must also come readily to equilibrium. Figure 14 shows equilibrium calculations for this reaction. At any temperature below 300°C, the equilibrium pressure of NO above BaCO₃/Ba(NO₃)₂ is much less than the concentration of NO in jet exhaust. Thus in this temperature range formation of BaCO₃ will be reversible and any BaO converted to BaCO₃ can still react with NO to form Ba(NO₃)₂.

c. Reaction of BaO with H₂O

The reaction BaO + H₂O → Ba(OH)₂ is also thermodynamically favorable but at temperatures below 300°C the equilibrium Ba(OH)₂ + 2 NO + 3/2 O₂ → Ba(NO₃)₂ + H₂O lies strongly to the right. Thus the arguments given above for the reaction of BaO with CO₂ apply to this case also. If the reaction of BaO with H₂O is slow relative to its reaction with NO, then Ba(OH)₂ will form, but this will be reversible and any BaO converted to Ba(OH)₂ can still react with NO to form Ba(NO₃)₂.

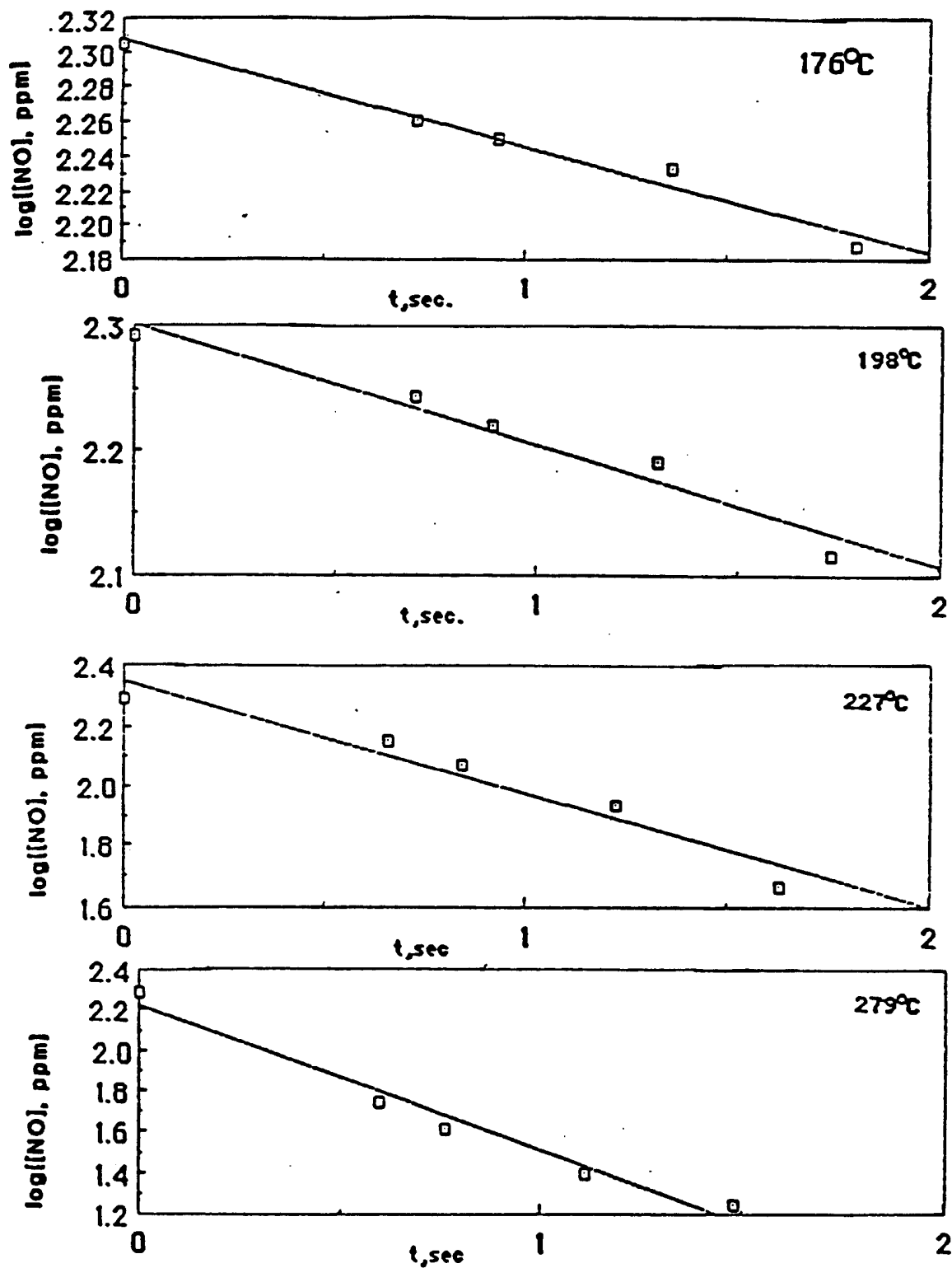


Figure 9. First-Order Rate Plots for Removal of NO by BaO at Various Initial Temperatures.

d. Possible Catalytic Reactions

In the discussion above it was implicitly assumed that all the NO that was removed from the flowing gas mixture was adsorbed by the BaO and that none was converted into N₂. Since N₂ was the principal component of the flowing gas mixture it would have been impossible to observe N₂ formation if it had occurred. It is also true that no attempt was made to observe a mass balance between NO adsorbed from the flowing gas mixture at one temperature and NO added to it at some higher temperature. Thus the assumption that NO was not being reduced to N₂ in these experiments is not addressed by experiment.

NO reduction, however, can occur in only two ways, selectively and nonselectively. Both kinds of reduction can happen only if a reducing agent is present. Selective reduction of NO occurs only with reducing agents that themselves contain nitrogen, i.e., reducing agents such as NH₃. The NO_x meter is sensitive to such materials and, as it did not detect their presence, they must be absent. Any of a wide range of reducing agents can cause nonselective reduction of NO, but (unless the reducing agent exhibits a high order of selectivity) there is a threshold for NO reduction: NO reduction begins only when the amount of reducing agent present exceeds that needed to consume all the O₂ present. In these experiments O₂ ranged from 1.1 to 20 percent, while the purity of the gases used exceeded 99.9 percent. Thus the amount of reducing agent needed to cause nonselective reduction could not have been present as an impurity. Consequently neither selective nor nonselective catalytic reduction of NO could have occurred in these experiments.

SECTION VI

CONCLUSIONS

A new, scientifically very interesting reaction has been discovered: the capture of NO by BaO_2 to form the nitrate. This reaction appears to satisfy all the requirements for a nearly ideal process to control NO_x emissions from jet engine test cells; *i.e.*, a NO_x -control process based on this reaction could be retrofitted into an existing jet engine test cell without requiring any change in normal cell operation. Further, using this new NO_x control process would require little or no attention from the personnel operating the jet engine test cell.

Of course these conclusions are based on a relatively brief laboratory scale study and hence are tentative. Both long-term testing and testing on a much larger scale will be necessary to develop this new process to the point that it may be considered available technology suitable for application to any test cell in need of controlling its NO_x emissions.

REFERENCES

1. Spicer, C.W., et al., Aircraft Emissions Characterizations, ESL-TR-87-63, Tyndall AFB, FL, March 1988.
2. Lyon, R.K., Method for the Reduction of the Concentration of NO from Combustion Effluents, U.S. Patent No. 3, 900, 554, August 1975.
3. Perry, R.A. and Siebers, D.L., "Rapid Reduction of Nitrogen Oxides in Exhaust Gas Streams," *Nature*, 324, 657 (1986).
4. Wicke, B.G., et al., "Cyanuric Acid + Nitrogen Oxide Reaction at 700°C and the Effects of Oxygen," Paper presented at the Western States Section, The Combustion Institute, October 17-18, 1988, Laguna Beach, CA.
5. Caton, J.A., and Siebers, D.L., "Removal of Nitric Oxide from Exhaust Gas with Cyanuric Acid, *Combustion and Flame*, 79, 31-46 (1990).
6. Perry, R.H., and Green, D., *Perry's Chemical Engineers' Handbook*, 6th Ed., McGraw-Hill, New York, 1984, pp. 4-37.
7. Moore, W.J., *Physical Chemistry*, 2nd Ed., Prentice-Hall, Inc., New York, 1955, p. 105.
8. Manufacturer's literature, "Merckquant 10020/10050 Nitrate Test" and "Merckquant 10007 Nitrite Test," E. Merck, Postfach 41 19, D-6100 Darmstadt 1, Federal Republic of Germany.
9. "NBS Tables of Chemical Thermodynamic Properties," *J. Phys. Chem. Ref. Data*, 11, Suppl. 2 (1982).
10. Moeller, T., *Inorganic Chemistry*, John Wiley & Sons, New York, 1953, p. 859.
11. Mitsuzawa, S., Method for Removing NO and SO₂ from Exhaust Gas, Japanese patent application, SHO 53 (1978) - 137891, application date 5/10/77, publication date 12/1/78.